

# Contents

Preface to the second edition

xix

Preface to the first edition

xxi

## Chapter 1 Origin of the Elements. Isotopes and Atomic Weights

1

1.1	Introduction	1
1.2	Origin of the Universe	1
1.3	Abundances of the Elements in the Universe	3
1.4	Stellar Evolution and the Spectral Classes of Stars	5
1.5	Synthesis of the Elements	9
1.5.1	Hydrogen burning	9
1.5.2	Helium burning and carbon burning	10
1.5.3	The $\alpha$ -process	11
1.5.4	The e-process (equilibrium process)	12
1.5.5	The s- and r-processes (slow and rapid neutron absorption)	12
1.5.6	The p-process (proton capture)	13
1.5.7	The x-process	13
1.6	Atomic Weights	15
1.6.1	Uncertainty in atomic weights	16
1.6.2	The problem of radioactive elements	18

## Chapter 2 Chemical Periodicity and the Periodic Table

20

2.1	Introduction	20
2.2	The Electronic Structure of Atoms	21
2.3	Periodic Trends in Properties	23
2.3.1	Trends in atomic and physical properties	23
2.3.2	Trends in chemical properties	27
2.4	Prediction of New Elements and Compounds	29

## Chapter 3 Hydrogen

32

3.1	Introduction	32
3.2	Atomic and Physical Properties of Hydrogen	34
3.2.1	Isotopes of hydrogen	34
3.2.2	<i>Ortho-</i> and <i>para</i> -hydrogen	35
3.2.3	Ionized forms of hydrogen	36
3.3	Preparation, Production and Uses	38
3.3.1	Hydrogen	38
3.3.2	Deuterium	39
3.3.3	Tritium	41
3.4	Chemical Properties and Trends	43
3.4.1	The coordination chemistry of hydrogen	44

3.5	Protonic Acids and Bases	48
3.6	The Hydrogen Bond	52
3.6.1	Influence on properties	53
3.6.2	Influence on structure	59
3.6.3	Strength of hydrogen bonds and theoretical description	61
3.7	Hydrides of the Elements	64
<b>Chapter 4</b>	<b>Lithium, Sodium, Potassium, Rubidium, Caesium and Francium</b>	<b>68</b>
4.1	Introduction	68
4.2	The Elements	68
4.2.1	Discovery and isolation	68
4.2.2	Terrestrial abundance and distribution	69
4.2.3	Production and uses of the metals	71
4.2.4	Properties of the alkali metals	74
4.2.5	Chemical reactivity and trends	76
4.2.6	Solutions in liquid ammonia and other solvents	77
4.3	Compounds	79
4.3.1	Introduction: the ionic-bond model	79
4.3.2	Halides and hydrides	82
4.3.3	Oxides, peroxides, superoxides and suboxides	84
4.3.4	Hydroxides	86
4.3.5	Oxoacid salts and other compounds	87
4.3.6	Coordination chemistry	90
4.3.7	Imides, amides and related compounds	99
4.3.8	Organometallic compounds	102
<b>Chapter 5</b>	<b>Beryllium, Magnesium, Calcium, Strontium, Barium and Radium</b>	<b>107</b>
5.1	Introduction	107
5.2	The Elements	108
5.2.1	Terrestrial abundance and distribution	108
5.2.2	Production and uses of the metals	110
5.2.3	Properties of the elements	111
5.2.4	Chemical reactivity and trends	112
5.3	Compounds	113
5.3.1	Introduction	113
5.3.2	Hydrides and halides	115
5.3.3	Oxides and hydroxides	119
5.3.4	Oxoacid salts and coordination complexes	122
5.3.5	Organometallic compounds	127
	Beryllium	127
	Magnesium	131
	Calcium, strontium and barium	136
<b>Chapter 6</b>	<b>Boron</b>	<b>139</b>
6.1	Introduction	139
6.2	Boron	140
6.2.1	Isolation and purification of the element	140
6.2.2	Structure of crystalline boron	141
6.2.3	Atomic and physical properties of boron	144
6.2.4	Chemical properties	144
6.3	Borides	145
6.3.1	Introduction	145
6.3.2	Preparation and stoichiometry	146
6.3.3	Structures of borides	147

## **Contents**

**vii**

6.4	Boranes (Boron Hydrides)	151
6.4.1	Introduction	151
6.4.2	Bonding and topology	157
6.4.3	Preparation and properties of boranes	162
6.4.4	The chemistry of small boranes and their anions ( $B_1$ – $B_4$ )	164
6.4.5	Intermediate-sized boranes and their anions ( $B_5$ – $B_9$ )	170
6.4.6	Chemistry of <i>nido</i> -decaborane, $B_{10}H_{14}$	173
6.4.7	Chemistry of <i>cis</i> - $B_nH_n^{2-}$	178
6.5	Carboranes	181
6.6	Metallocarboranes	189
6.7	Boron Halides	195
6.7.1	Boron trihalides	195
6.7.2	Lower halides of boron	200
6.8	Boron–Oxygen Compounds	203
6.8.1	Boron oxides and oxoacids	203
6.8.2	Borates	205
6.8.3	Organic compounds containing boron–oxygen bonds	207
6.9	Boron–Nitrogen Compounds	207
6.10	Other Compounds of Boron	211
6.10.1	Compounds with bonds to P, As or Sb	211
6.10.2	Compounds with bonds to S, Se and Te	213

## **Chapter 7**

### **Aluminium, Gallium, Indium and Thallium**

**216**

7.1	Introduction	216
7.2	The Elements	217
7.2.1	Terrestrial abundance and distribution	217
7.2.2	Preparation and uses of the metals	219
7.2.3	Properties of the elements	222
7.2.4	Chemical reactivity and trends	224
7.3	Compounds	227
7.3.1	Hydrides and related complexes	227
7.3.2	Halides and halide complexes	233
	Aluminium trihalides	233
	Trihalides of gallium, indium and thallium	237
	Lower halides of gallium, indium and thallium	240
7.3.3	Oxides and hydroxides	242
7.3.4	Ternary and more complex oxide phases	247
	Spinels and related compounds	247
	Sodium- $\beta$ -alumina and related phases	249
	Tricalcium aluminate, $Ca_3Al_2O_6$	251
7.3.5	Other inorganic compounds	252
	Chalcogenides	252
	Compounds with bonds to N, P, As, Sb or Bi	255
	Some unusual stereochemistries	256
7.3.6	Organometallic compounds	257
	Organoaluminium compounds	258
	Organometallic compounds of Ga, In and Tl	262
	Al–N heterocycles and clusters	265

## **Chapter 8**

### **Carbon**

**268**

8.1	Introduction	268
8.2	Carbon	269
8.2.1	Terrestrial abundance and distribution	269
8.2.2	Allotropic forms	274
8.2.3	Atomic and physical properties	276
8.2.4	Fullerenes	278
	Structure of the fullerenes	280
	Other molecular allotropes of carbon	282
	Chemistry of the fullerenes	282
	Reduction of fullerenes to fullerides	285

	Addition reactions	286
	Heteroatom fullerene-type clusters	287
	Encapsulation of metal atoms by fullerene clusters	288
8.2.5	Chemical properties of carbon	289
8.3	Graphite Intercalation Compounds	293
8.4	Carbides	296
	Metallocarbohedrenes (met-cars)	300
8.5	Hydrides, Halides and Oxohalides	301
8.6	Oxides and Carbonates	305
8.7	Chalcogenides and Related Compounds	313
8.8	Cyanides and Other Carbon–Nitrogen Compounds	319
8.9	Organometallic Compounds	326
<b>Chapter 9</b>	<b>Silicon</b>	<b>328</b>
9.1	Introduction	328
9.2	Silicon	329
	9.2.1 Occurrence and distribution	329
	9.2.2 Isolation, production and industrial uses	330
	9.2.3 Atomic and physical properties	330
	9.2.4 Chemical properties	331
9.3	Compounds	335
	9.3.1 Silicides	335
	9.3.2 Silicon hydrides (silanes)	337
	9.3.3 Silicon halides and related complexes	340
	9.3.4 Silica and silicic acids	342
	9.3.5 Silicate minerals	347
	Silicates with discrete units	347
	Silicates with chain or ribbon structures	349
	Silicates with layer structures	349
	Silicates with framework structures	354
	9.3.6 Other inorganic compounds of silicon	359
	9.3.7 Organosilicon compounds and silicones	361
<b>Chapter 10</b>	<b>Germanium, Tin and Lead</b>	<b>367</b>
10.1	Introduction	367
10.2	The Elements	368
	10.2.1 Terrestrial abundance and distribution	368
	10.2.2 Production and uses of the elements	369
	10.2.3 Properties of the elements	371
	10.2.4 Chemical reactivity and group trends	373
10.3	Compounds	374
	10.3.1 Hydrides and hydrohalides	374
	10.3.2 Halides and related complexes	375
	Germanium halides	376
	Tin halides	377
	Lead halides	381
	10.3.3 Oxides and hydroxides	382
	10.3.4 Derivatives of oxoacids	387
	10.3.5 Other inorganic compounds	389
	10.3.6 Metal–metal bonds and clusters	391
	10.3.7 Organometallic compounds	396
	Germanium	396
	Tin	399
	Lead	404
<b>Chapter 11</b>	<b>Nitrogen</b>	<b>406</b>
11.1	Introduction	406

## Contents

**ix**

11.2	The Element	407
11.2.1	Abundance and distribution	407
11.2.2	Production and uses of nitrogen	409
11.2.3	Atomic and physical properties	411
11.2.4	Chemical reactivity	412
11.3	Compounds	416
11.3.1	Nitrides, azides and nitrido complexes	417
11.3.2	Ammonia and ammonium salts	420
	Liquid ammonia as a solvent	424
11.3.3	Other hydrides of nitrogen	426
	Hydrazine	427
	Hydroxylamine	431
	Hydrogen azide	432
11.3.4	Thermodynamic relations between N-containing species	434
11.3.5	Nitrogen halides and related compounds	438
11.3.6	Oxides of nitrogen	443
	Nitrous oxide, $\text{N}_2\text{O}$	443
	Nitric oxide, NO	445
	Dinitrogen trioxide, $\text{N}_2\text{O}_3$	454
	Nitrogen dioxide, $\text{NO}_2$ , and dinitrogen tetroxide, $\text{N}_2\text{O}_4$	455
	Dinitrogen pentoxide, $\text{N}_2\text{O}_5$ , and nitrogen trioxide, $\text{NO}_3$	458
11.3.7	Oxoacids, oxoanions and oxoacid salts of nitrogen	459
	Hyponitrous acid and hyponitrites	459
	Nitrous acid and nitrates	461
	Nitric acid and nitrates	465
	Orthonitrates, $\text{M}_3^{\text{I}}\text{NO}_4$	471

## Chapter 12 Phosphorus

**473**

12.1	Introduction	473
12.2	The Element	475
12.2.1	Abundance and distribution	475
12.2.2	Production and uses of elemental phosphorus	479
12.2.3	Allotropes of phosphorus	479
12.2.4	Atomic and physical properties	482
12.2.5	Chemical reactivity and stereochemistry	483
12.3	Compounds	489
12.3.1	Phosphides	489
12.3.2	Phosphine and related compounds	492
12.3.3	Phosphorus halides	495
	Phosphorus trihalides	495
	Diphosphorus tetrahalides and other lower halides of phosphorus	497
	Phosphorus pentahalides	498
	Pseudohalides of phosphorus(III)	501
12.3.4	Oxohalides and thiohalides of phosphorus	501
12.3.5	Phosphorus oxides, sulfides, selenides and related compounds	503
	Oxides	503
	Sulfides	506
	Oxosulfides	510
12.3.6	Oxoacids of phosphorus and their salts	510
	Hypophosphorous acid and hypophosphites [ $\text{H}_2\text{PO}(\text{OH})$ and $\text{H}_2\text{PO}_2^-$ ]	513
	Phosphorous acid and phosphites [ $\text{HPO}(\text{OH})_2$ and $\text{HPO}_3^{2-}$ ]	514
	Hypophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_6$ ) and hypophosphates	515
	Other lower oxoacids of phosphorus	516
	The phosphoric acids	516
	Orthophosphates	523
	Chain polyphosphates	526
	Cyclo-polyphosphoric acids and cyclo-polyphosphates	529
12.3.7	Phosphorus–nitrogen compounds	531
	Cyclophosphazanes	533
	Phosphazenes	534

**Contents**

Polyphosphazenes	536
Applications	542
12.3.8 Organophosphorus compounds	542

**Chapter 13 Arsenic, Antimony and Bismuth****547**

13.1 Introduction	547
13.2 The Elements	548
13.2.1 Abundance, distribution and extraction	548
13.2.2 Atomic and physical properties	550
13.2.3 Chemical reactivity and group trends	552
13.3 Compounds of Arsenic, Antimony and Bismuth	554
13.3.1 Intermetallic compounds and alloys	554
13.3.2 Hydrides of arsenic, antimony and bismuth	557
13.3.3 Halides and related complexes	558
Trihalides, $\text{MX}_3$	558
Pentahalides, $\text{MX}_5$	561
Mixed halides and lower halides	563
Halide complexes of $\text{M}^{\text{III}}$ and $\text{M}^{\text{V}}$	564
Oxide halides	570
13.3.4 Oxides and oxo compounds	572
Oxo compounds of $\text{M}^{\text{III}}$	573
Mixed-valence oxides	576
Oxo compounds of $\text{M}^{\text{V}}$	576
13.3.5 Sulfides and related compounds	578
13.3.6 Metal–metal bonds and clusters	583
13.3.7 Other inorganic compounds	591
13.3.8 Organometallic compounds	592
Organoarsenic(III) compounds	593
Organoarsenic(V) compounds	594
Physiological activity of arsenicals	596
Organoantimony and organobismuth compounds	596

**Chapter 14 Oxygen****600**

14.1 The Element	600
14.1.1 Introduction	600
14.1.2 Occurrence	602
14.1.3 Preparation	603
14.1.4 Atomic and physical properties	604
14.1.5 Other forms of oxygen	607
Ozone	607
Atomic oxygen	611
14.1.6 Chemical properties of dioxygen, $\text{O}_2$	612
14.2 Compounds of Oxygen	615
14.2.1 Coordination chemistry: dioxygen as a ligand	615
14.2.2 Water	620
Introduction	620
Distribution and availability	621
Physical properties and structure	623
Water of crystallization, aquo complexes and solid hydrates	625
Chemical properties	627
Polywater	632
14.2.3 Hydrogen peroxide	633
Physical properties	633
Chemical properties	634
14.2.4 Oxygen fluorides	638
14.2.5 Oxides	640
Various methods of classification	640
Nonstoichiometry	642

**Chapter 15 Sulfur****645**

15.1	The Element	645
15.1.1	Introduction	645
15.1.2	Abundance and distribution	647
15.1.3	Production and uses of elemental sulfur	649
15.1.4	Allotropes of sulfur	652
15.1.5	Atomic and physical properties	661
15.1.6	Chemical reactivity	662
	Polyatomic sulfur cations	664
	Sulfur as a ligand	665
	Other ligands containing sulfur as donor atom	673
15.2	Compounds of Sulfur	676
15.2.1	Sulfides of the metallic elements	676
	General considerations	676
	Structural chemistry of metal sulfides	679
	Anionic polysulfides	681
15.2.2	Hydrides of sulfur (sulfanes)	682
15.2.3	Halides of sulfur	683
	Sulfur fluorides	683
	Chlorides, bromides and iodides of sulfur	689
15.2.4	Oxohalides of sulfur	693
15.2.5	Oxides of sulfur	695
	Lower oxides	695
	Sulfur dioxide, $\text{SO}_2$	698
	Sulfur dioxide as a ligand	701
	Sulfur trioxide	703
	Higher oxides	704
15.2.6	Oxoacids of sulfur	706
	Sulfuric acid, $\text{H}_2\text{SO}_4$	710
	Peroxosulfuric acids, $\text{H}_2\text{SO}_5$ and $\text{H}_2\text{S}_2\text{O}_8$	712
	Thiosulfuric acid, $\text{H}_2\text{S}_2\text{O}_3$	714
	Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$	715
	Polythionic acids, $\text{H}_2\text{S}_n\text{O}_6$	716
	Sulfurous acid, $\text{H}_2\text{SO}_3$	717
	Disulfurous acid, $\text{H}_2\text{S}_2\text{O}_5$	720
	Dithionous acid, $\text{H}_2\text{S}_2\text{O}_4$	720
15.2.7	Sulfur–nitrogen compounds	721
	Binary sulfur nitrides	722
	Sulfur–nitrogen cations and anions	730
	Sulfur imides, $\text{S}_{8-n}(\text{NH})_n$	735
	Other cyclic sulfur–nitrogen compounds	736
	Sulfur–nitrogen–halogen compounds	736
	Sulfur–nitrogen–oxygen compounds	740

**Chapter 16 Selenium, Tellurium and Polonium****747**

16.1	The Elements	747
16.1.1	Introduction: history, abundance, distribution	747
16.1.2	Production and uses of the elements	748
16.1.3	Allotropy	751
16.1.4	Atomic and physical properties	753
16.1.5	Chemical reactivity and trends	754
16.1.6	Polyatomic cations, $\text{M}_x^{n+}$	759
16.1.7	Polyatomic anions, $\text{M}_x^{2-}$	762
16.2	Compounds of Selenium, Tellurium and Polonium	765
16.2.1	Selenides, tellurides and polonides	765
16.2.2	Hydrides	766
16.2.3	Halides	767
	Lower halides	768
	Tetrahalides	772

Hexahalides	775
Halide complexes	776
16.2.4 Oxohalides and pseudohalides	777
16.2.5 Oxides	779
16.2.6 Hydroxides and oxoacids	781
16.2.7 Other inorganic compounds	783
16.2.8 Organo-compounds	786

**Chapter 17 The Halogens: Fluorine, Chlorine, Bromine, Iodine and Astatine** 789

17.1 The Elements	789
17.1.1 Introduction	789
Fluorine	789
Chlorine	792
Bromine	793
Iodine	794
Astatine	794
17.1.2 Abundance and distribution	795
17.1.3 Production and uses of the elements	796
17.1.4 Atomic and physical properties	800
17.1.5 Chemical reactivity and trends	804
General reactivity and stereochemistry	804
Solutions and charge-transfer complexes	806
17.2 Compounds of Fluorine, Chlorine, Bromine and Iodine	809
17.2.1 Hydrogen halides, HX	809
Preparation and uses	809
Physical properties of the hydrogen halides	812
Chemical reactivity of the hydrogen halides	813
The hydrogen halides as nonaqueous solvents	816
17.2.2 Halides of the elements	819
Fluorides	820
Chlorides, bromides and iodides	821
17.2.3 Interhalogen compounds	824
Diatomeric interhalogens, XY	824
Tetra-atomic interhalogens, XY <sub>3</sub>	828
Hexa-atomic and octa-atomic interhalogens, XF <sub>5</sub> and IF <sub>7</sub>	832
17.2.4 Polyhalide anions	835
17.2.5 Polyhalonium cations XY <sub>2n</sub> <sup>+</sup>	839
17.2.6 Halogen cations	842
17.2.7 Oxides of chlorine, bromine and iodine	844
Oxides of chlorine	844
Oxides of bromine	850
Oxides of iodine	851
17.2.8 Oxoacids and oxoacid salts	853
General considerations	853
Hypohalous acids, HOX, and hypohalites, XO <sup>-</sup>	856
Halous acids, HOXO, and halites, XO <sub>2</sub> <sup>-</sup>	859
Halic acids, HOXO <sub>2</sub> , and halates, XO <sub>3</sub> <sup>-</sup>	862
Perhalic acid and perhalates	865
Perchloric acid and perchlorates	865
Perbromic acid and perbromates	871
Periodic acids and periodates	872
17.2.9 Halogen oxide fluorides and related compounds	875
Chlorine oxide fluorides	875
Bromine oxide fluorides	880
Iodine oxide fluorides	881
17.2.10 Halogen derivatives of oxoacids	883
17.3 The Chemistry of Astatine	885

<b>Chapter 18</b>	<b>The Noble Gases: Helium, Neon, Argon, Krypton, Xenon and Radon</b>	<b>888</b>
18.1	Introduction	888
18.2	The Elements	889
18.2.1	Distribution, production and uses	889
18.2.2	Atomic and physical properties of the elements	890
18.3	Chemistry of the Noble Gases	892
18.3.1	Clathrates	893
18.3.2	Compounds of xenon	893
18.3.3	Compounds of other noble gases	903
<b>Chapter 19</b>	<b>Coordination and Organometallic Compounds</b>	<b>905</b>
19.1	Introduction	905
19.2	Types of Ligand	906
19.3	Stability of Coordination Compounds	908
19.4	The Various Coordination Numbers	912
19.5	Isomerism	918
19.5.1	Conformational isomerism	918
19.5.2	Geometrical isomerism	919
19.5.3	Optical isomerism	919
19.5.4	Ionization isomerism	920
19.5.5	Linkage isomerism	920
19.5.6	Coordination isomerism	920
19.5.7	Polymerization isomerism	921
19.5.8	Ligand isomerism	921
19.6	The Coordinate Bond	921
19.7	Organometallic Compounds	924
19.7.1	Monohapto ligands	925
19.7.2	Dihapto ligands	930
19.7.3	Trihapto ligands	933
19.7.4	Tetrahapto ligands	935
19.7.5	Pentahapto ligands	937
19.7.6	Hexahapto ligands	940
19.7.7	Heptahapto and octahapto ligands	941
<b>Chapter 20</b>	<b>Scandium, Yttrium, Lanthanum and Actinium</b>	<b>944</b>
20.1	Introduction	944
20.2	The Elements	945
20.2.1	Terrestrial abundance and distribution	945
20.2.2	Preparation and uses of the metals	945
20.2.3	Properties of the elements	946
20.2.4	Chemical reactivity and trends	948
20.3	Compounds of Scandium, Yttrium, Lanthanum and Actinium	949
20.3.1	Simple compounds	949
20.3.2	Complexes	950
20.3.3	Organometallic compounds	953
<b>Chapter 21</b>	<b>Titanium, Zirconium and Hafnium</b>	<b>954</b>
21.1	Introduction	954
21.2	The Elements	955
21.2.1	Terrestrial abundance and distribution	955
21.2.2	Preparation and uses of the metals	955
21.2.3	Properties of the elements	956
21.2.4	Chemical reactivity and trends	958
21.3	Compounds of Titanium, Zirconium and Hafnium	961
21.3.1	Oxides and sulfides	961

21.3.2	Mixed (or complex) oxides	962
21.3.3	Halides	964
21.3.4	Compounds with oxoanions	966
21.3.5	Complexes	967
	Oxidation state IV ( $d^0$ )	967
	Oxidation state III ( $d^1$ )	969
	Lower oxidation states	971
21.3.6	Organometallic compounds	972
<b>Chapter 22</b>	<b>Vanadium, Niobium and Tantalum</b>	<b>976</b>
22.1	Introduction	976
22.2	The Elements	977
22.2.1	Terrestrial abundance and distribution	977
22.2.2	Preparation and uses of the metals	977
22.2.3	Atomic and physical properties of the elements	978
22.2.4	Chemical reactivity and trends	979
22.3	Compounds of Vanadium, Niobium and Tantalum	981
22.3.1	Oxides	981
22.3.2	Polymetallates	983
22.3.3	Sulfides, selenides and tellurides	987
22.3.4	Halides and oxohalides	988
22.3.5	Compounds with oxoanions	993
22.3.6	Complexes	994
	Oxidation state V ( $d^0$ )	994
	Oxidation state IV ( $d^1$ )	994
	Oxidation state III ( $d^2$ )	996
	Oxidation state II ( $d^3$ )	998
22.3.7	The biochemistry of vanadium	999
22.3.8	Organometallic compounds	999
<b>Chapter 23</b>	<b>Chromium, Molybdenum and Tungsten</b>	<b>1002</b>
23.1	Introduction	1002
23.2	The Elements	1003
23.2.1	Terrestrial abundance and distribution	1003
23.2.2	Preparation and uses of the metals	1003
23.2.3	Properties of the elements	1004
23.2.4	Chemical reactivity and trends	1005
23.3	Compounds of Chromium, Molybdenum and Tungsten	1007
23.3.1	Oxides	1007
23.3.2	Isopolymetallates	1009
23.3.3	Heteropolymetallates	1013
23.3.4	Tungsten and molybdenum bronzes	1016
23.3.5	Sulfides, selenides and tellurides	1017
23.3.6	Halides and oxohalides	1019
23.3.7	Complexes of chromium, molybdenum and tungsten	1023
	Oxidation state VI ( $d^0$ )	1023
	Oxidation state V ( $d^1$ )	1024
	Oxidation state IV ( $d^2$ )	1025
	Oxidation state III ( $d^3$ )	1027
	Oxidation state II ( $d^4$ )	1031
23.3.8	Biological activity and nitrogen fixation	1035
23.3.9	Organometallic compounds	1037
<b>Chapter 24</b>	<b>Manganese, Technetium and Rhenium</b>	<b>1040</b>
24.1	Introduction	1040
24.2	The Elements	1041

## Contents

**xv**

24.2.1	Terrestrial abundance and distribution	1041
24.2.2	Preparation and uses of the metals	1041
24.2.3	Properties of the elements	1043
24.2.4	Chemical reactivity and trends	1044
24.3	Compounds of Manganese, Technetium and Rhenium	1045
24.3.1	Oxides and chalcogenides	1045
24.3.2	Oxoanions	1049
24.3.3	Halides and oxohalides	1051
24.3.4	Complexes of manganese, technetium and rhenium	1054
	Oxidation state VII ( $d^0$ )	1054
	Oxidation state VI ( $d^1$ )	1055
	Oxidation state V ( $d^2$ )	1055
	Oxidation state IV ( $d^3$ )	1056
	Oxidation state III ( $d^4$ )	1057
	Oxidation state II ( $d^5$ )	1058
	Lower oxidation states	1061
24.3.5	The biochemistry of manganese	1061
24.3.6	Organometallic compounds	1062

## **Chapter 25 Iron, Ruthenium and Osmium**

**1070**

25.1	Introduction	1070
25.2	The Elements Iron, Ruthenium and Osmium	1071
25.2.1	Terrestrial abundance and distribution	1071
25.2.2	Preparation and uses of the elements	1071
25.2.3	Properties of the elements	1074
25.2.4	Chemical reactivity and trends	1075
25.3	Compounds of Iron, Ruthenium and Osmium	1079
25.3.1	Oxides and other chalcogenides	1079
25.3.2	Mixed metal oxides and oxoanions	1081
25.3.3	Halides and oxohalides	1082
25.3.4	Complexes	1085
	Oxidation state VIII ( $d^0$ )	1085
	Oxidation state VII ( $d^1$ )	1085
	Oxidation state VI ( $d^2$ )	1085
	Oxidation state V ( $d^3$ )	1086
	Oxidation state IV ( $d^4$ )	1086
	Oxidation state III ( $d^5$ )	1088
	Oxidation state II ( $d^6$ )	1091
	Mixed valence compounds of ruthenium	1097
	Lower oxidation states	1098
25.3.5	The biochemistry of iron	1098
	Haemoglobin and myoglobin	1099
	Cytochromes	1101
	Iron-sulfur proteins	1102
25.3.6	Organometallic compounds	1104
	Carbonyls	1104
	Carbonyl hydrides and carbonylate anions	1105
	Carbonyl halides and other substituted carbonyls	1108
	Ferrocene and other cyclopentadienyls	1109

## **Chapter 26 Cobalt, Rhodium and Iridium**

**1113**

26.1	Introduction	1113
26.2	The Elements	1113
26.2.1	Terrestrial abundance and distribution	1113
26.2.2	Preparation and uses of the elements	1114
26.2.3	Properties of the elements	1115
26.2.4	Chemical reactivity and trends	1116
26.3	Compounds of Cobalt, Rhodium and Iridium	1117

26.3.1	Oxides and sulfides	1117
26.3.2	Halides	1119
26.3.3	Complexes	1121
	Oxidation state IV ( $d^5$ )	1121
	Oxidation state III ( $d^6$ )	1122
	Oxidation state II ( $d^7$ )	1129
	Oxidation state I ( $d^8$ )	1133
	Lower oxidation states	1137
26.3.4	The biochemistry of cobalt	1138
26.3.5	Organometallic compounds	1139
	Carbonyls	1140
	Cyclopentadienyls	1143

**Chapter 27 Nickel, Palladium and Platinum****1144**

27.1	Introduction	1144
27.2	The Elements	1145
27.2.1	Terrestrial abundance and distribution	1145
27.2.2	Preparation and uses of the elements	1145
27.2.3	Properties of the elements	1148
27.2.4	Chemical reactivity and trends	1149
27.3	Compounds of Nickel, Palladium and Platinum	1150
27.3.1	The Pd/H <sub>2</sub> system	1150
27.3.2	Oxides and chalcogenides	1151
27.3.3	Halides	1152
27.3.4	Complexes	1154
	Oxidation state IV ( $d^6$ )	1154
	Oxidation state III ( $d^7$ )	1155
	Oxidation state II ( $d^8$ )	1156
	Oxidation state I ( $d^9$ )	1166
	Oxidation state 0 ( $d^{10}$ )	1166
27.3.5	The biochemistry of nickel	1167
27.3.6	Organometallic compounds	1167
	$\sigma$ -Bonded compounds	1167
	Carbonyls	1168
	Cyclopentadienyls	1170
	Alkene and alkyne complexes	1170
	$\pi$ -Allylic complexes	1171

**Chapter 28 Copper, Silver and Gold****1173**

28.1	Introduction	1173
28.2	The Elements	1174
28.2.1	Terrestrial abundance and distribution	1174
28.2.2	Preparation and uses of the elements	1174
28.2.3	Atomic and physical properties of the elements	1176
28.2.4	Chemical reactivity and trends	1177
28.3	Compounds of Copper, Silver and Gold	1180
28.3.1	Oxides and sulfides	1181
28.3.2	High temperature superconductors	1182
28.3.3	Halides	1183
28.3.4	Photography	1185
28.3.5	Complexes	1187
	Oxidation state III ( $d^8$ )	1187
	Oxidation state II ( $d^9$ )	1189
	Electronic spectra and magnetic properties of copper(II)	1193
	Oxidation state I ( $d^{10}$ )	1194
	Gold cluster compounds	1197
28.3.6	Biochemistry of copper	1197
28.3.7	Organometallic compounds	1199

<b>Chapter 29 Zinc, Cadmium and Mercury</b>	<b>1201</b>
29.1 Introduction	1201
29.2 The Elements	1202
29.2.1 Terrestrial abundance and distribution	1202
29.2.2 Preparation and uses of the elements	1202
29.2.3 Properties of the elements	1203
29.2.4 Chemical reactivity and trends	1205
29.3 Compounds of Zinc, Cadmium and Mercury	1208
29.3.1 Oxides and chalcogenides	1208
29.3.2 Halides	1211
29.3.3 Mercury(I)	1213
Polycation of mercury	1214
29.3.4 Zinc(II) and cadmium(II)	1215
29.3.5 Mercury(II)	1217
Hg <sup>II</sup> -N compounds	1218
Hg <sup>II</sup> -S compounds	1220
Cluster compounds involving mercury	1220
29.3.6 Organometallic compounds	1221
29.3.7 Biological and environmental importance	1224
<b>Chapter 30 The Lanthanide Elements (<math>Z = 58\text{--}71</math>)</b>	<b>1227</b>
30.1 Introduction	1227
30.2 The Elements	1229
30.2.1 Terrestrial abundance and distribution	1229
30.2.2 Preparation and uses of the elements	1230
30.2.3 Properties of the elements	1232
30.2.4 Chemical reactivity and trends	1235
30.3 Compounds of the Lanthanides	1238
30.3.1 Oxides and chalcogenides	1238
30.3.2 Halides	1240
30.3.3 Magnetic and spectroscopic properties	1242
30.3.4 Complexes	1244
Oxidation state IV	1244
Oxidation state III	1245
Oxidation state II	1248
30.3.5 Organometallic compounds	1248
Cyclopentadienides and related compounds	1248
Alkyls and aryls	1249
<b>Chapter 31 The Actinide and Transactinide Elements (<math>Z = 90\text{--}112</math>)</b>	<b>1250</b>
31.1 Introduction	1250
Superheavy elements	1253
31.2 The Actinide Elements	1253
31.2.1 Terrestrial abundance and distribution	1253
31.2.2 Preparation and uses of the actinide elements	1255
Nuclear reactors and atomic energy	1256
Nuclear fuel reprocessing	1260
31.2.3 Properties of the actinide elements	1262
31.2.4 Chemical reactivity and trends	1264
31.3 Compounds of the Actinides	1267
31.3.1 Oxides and chalcogenides of the actinides	1268
31.3.2 Mixed metal oxides	1269
31.3.3 Halides of the actinide elements	1269
31.3.4 Magnetic and spectroscopic properties	1272
31.3.5 Complexes of the actinide elements	1273
Oxidation state VII	1273
Oxidation state VI	1273
Oxidation state V	1274
Oxidation state IV	1275

Oxidation state III	1277
Oxidation state II	1278
31.3.6 Organometallic compounds of the actinides	1278
31.4 The Transactinide Elements	1280
31.4.1 Introduction	1280
31.4.2 Element 104	1281
31.4.3 Element 105	1282
31.4.4 Element 106	1282
31.4.5 Elements 107, 108 and 109	1283
31.4.6 Elements 110, 111 and 112	1283
<b>Appendix 1 Atomic Orbitals</b>	<b>1285</b>
<b>Appendix 2 Symmetry Elements, Symmetry Operations and Point Groups</b>	<b>1290</b>
<b>Appendix 3 Some Non-SI Units</b>	<b>1293</b>
<b>Appendix 4 Abundance of Elements in Crustal Rocks</b>	<b>1294</b>
<b>Appendix 5 Effective Ionic Radii</b>	<b>1295</b>
<b>Appendix 6 Nobel Prize for Chemistry</b>	<b>1296</b>
<b>Appendix 7 Nobel Prize for Physics</b>	<b>1300</b>
<b>Index</b>	<b>1305</b>